

Significance of logarithmic throwing index: a theoretical approach

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An expression for the metal distribution ratio in electroplating systems as a function of the primary current density ratio L in the form $M = L [W(1 - r)/(1 + K)]$ is derived. W , r and K are three dimensionless parameters related to the current efficiency ratio, the concentration polarization and activation polarization during the metal discharge. The function $[W(1 - r)/(1 + K)]$ is compared with $1/A$, the logarithmic throwing index empirically determined by Chin. The metal distribution ratio calculated by the use of the above formula is compared with the experimentally observed values. The close agreement between the two within an accuracy of 10% proves the validity of the equation derived. The logarithmic throwing power of electroplating systems is thus confirmed on theoretical grounds.

Nomenclature

A = Logarithmic Throwing Index – inverse of the slope of the plot of $\log M$ versus $\log L$

b = Tafel slope. Slope of the equation $\eta = a + b \log i$

d_n = Current efficiency in percent for metal deposition at near cathode

d_f = Current efficiency in percent for metal deposition at far cathode

E = The overall cell potential

E_n = The potential drop in the electrolyte between the anode and near cathode

E_f = The potential drop in the electrolyte between the anode and far cathode

e_a = Dynamic anode potential

e_n = Dynamic potential at the near cathode at a current density i'_n

e_f = Dynamic potential at the far cathode at a current density i'_f

f = a fraction = $\frac{i_L - i'_n}{i_L - i'_f}$

i = The average current density ($A \text{ dm}^{-2}$)

i_n = The primary current density at the near cathode when there is no polarization ($A \text{ dm}^{-2}$)

i_f = The primary current density at the far cathode when there is no polarization ($A \text{ dm}^{-2}$)

i'_n = The secondary current density at the near cathode ($A \text{ dm}^{-2}$)

i'_f = The secondary current density at the far cathode ($A \text{ dm}^{-2}$)

i_{H_n} = The partial cathode current density at the near cathode for parallel cathodic reactions other than metal discharge ($A \text{ dm}^{-2}$)

i_{H_f} = The partial cathode current density at the far cathode for parallel cathodic reactions other than metal discharge ($A \text{ dm}^{-2}$)

i_{M_n} = The partial cathode current density for metal discharge at the near cathode

i_{M_f} = The partial cathode current density for metal discharge at the far cathode

K = A dimensionless parameter = $b/2.3 E_f$

L = Linear Ratio = i'_f/l_n or i_n/i'_f

l_n = Linear distance of the near cathode (cm)

l_f = Linear distance of the far cathode (cm)

M = Metal distribution ratio

m_n = Weight of metal deposited on the near cathode

m_f = Weight of metal deposited on the far cathode

R = Secondary current distribution ratio = i'_n/i'_f

r = A dimensionless parameter related to K and f and given by $f = (1/L)^{r/K}$

W = A dimensionless parameter related current efficiency ratio $R^{W-1} = d_n/d_f$

- ρ = Specific resistivity of the electrolyte ($\Omega \text{ cm}^{-2}$)
 η_n = The overpotential at the near cathode (V)
 η_f = The overpotential at the far cathode
 i_0 = The exchange current density

1. Introduction

The primary current distribution over an electrode in an electrolytic cell is solely determined by the cell geometry, the cell size, the shape and the position of the electrodes in the cell. In electroplating, the amount of metal deposited on an area will be proportional to primary current density on that area provided there is equal or no polarization and the current efficiency for metal deposition is 100%. But in practice, the actual current distribution over the electrode tends to become more uniform because of the influence of polarization effects and varying current efficiencies with the changes in the primary current distribution over the area.

1.1. Formulae for throwing power

Several methods have been used to measure what is termed as 'Throwing Power' of the plating baths and a number of formulae [1-6] have been proposed to express this throwing power (Table 1).

Table 1. Various formulae for throwing power

Haring [1]	$(L - M)/L$
Heatley-Pan [2]	$(L - M)/(L - 1)$
Field [3]	$(L - M)/(L + M - 2)$
Subramanian [5]	$(L - M)/M(L - 1)$
Jelenick & David [4]	$M = mL + C$ 1/m is known as Throwing Index (Linear)
Gardam [7]	$T = 1/i + 2il_n/N$ where $N = b/2\rho$ N is known as Throwing Number
Chin [13]	$M = L(1/A)$ or $\log M = (1/A) \log L$ A is termed Logarithmic Throwing Index

Most of these formulae are empirical, and the values so expressed are related to a particular geometry of the cell. The Haring-Blum cell is the one most commonly used in the determination of the throwing power even though its limitations have

been discussed by many authors [7-10]. Recently, Chey and Wan [11] have developed three methods of approximation to predict metal distribution in electroplating systems. As it is desirable to have a single-valued parameter to express the capability of an electroplating bath for metal distribution over a range of Linear Ratios, Jelenick and David [4] derived the Linear Throwing Index. The limitations of the Linear Throwing index was dealt with by Watson [12], Subramanian [5] and recently by Chin [13]. Chin has proposed a 'logarithmic throwing index' as a measure of throwing power. He found that among several functions tested, the equation

$$M = L^{1/A} \quad (1)$$

gave the best fit to the experimental data and still retained the characteristics of a single-valued parameter. However, in conclusion he stated 'The method is proposed principally as an empirical tool to minimize the experimental effort required for electroplating studies. It is felt that further theoretical study is necessary to clarify why the throwing power of plating baths follows the logarithmic fashion as suggested by Equation (1)'.

1.2. Objective of the present paper

The present paper describes one such attempt to explain why the throwing power of plating baths follows the logarithmic fashion as found by Chin. An equation for the metal distribution has been derived which is of the form of Equation 1 where A is found to be a function the specific resistance of the electrolyte, the average current density, the current efficiency for the metal discharge, its limiting current density and the Tafel slope.

2. Theoretical derivation of the equation $M = L^{1/A}$

A Haring Cell with two cathodes and a gauze anode with a large area placed in between the cathodes as described by Haring and Blum [1] is used for the derivation of the equation. It is evident that the cell voltage is

$$E = e_a + \rho l_n i_n + e_n = e_a + \rho l_f i_f + e_f \quad (2)$$

Table 2. Percentage error due to the approximation $a^x = 1 + 2.3 x \log a$

a	$x = 0.2$			$x = 0.1$			$x = 0.05$		
	$(1 + Y)$	R_3^2	Error (%)	$(1 + Y)$	R_3^2	Error (%)	$(1 + Y)$	R_3^2	Error (%)
20	1.5986	0.4463	27.71	1.2992	0.06389	4.917	1.1496	0.0131	1.139
10	1.46	0.196	13.43	1.23	0.04085	3.322	1.115	0.0075	0.673
5	1.3215	0.07617	5.763	1.1608	0.01541	1.327	1.0804	0.0009	0.083

2.1. Primary current distribution ratio L

When there is no or negligible polarization at the cathodes and if e_a is negligibly small, Equation 2 reduces to

$$\rho l_n i_n = \rho l_f i_f \quad (3)$$

i.e.

$$(i_n/i_f) = (l_f/l_n) = L. \quad (4)$$

2.2. Secondary current distribution R

In practical plating, there will be polarization at the cathodes and it will be a function of the current densities at the cathodes. Now, if i'_n and i'_f are the current densities at the near and the far cathodes respectively, due to secondary current distribution, then

$$E = e_a + \rho l_n i'_n + e_n = e_a + \rho l_f i'_f + e_f \quad (5)$$

with e_a small and equal on both sides,

$$\rho l_n i'_n + e_n = \rho l_f i'_f + e_f \quad (6)$$

$$\rho l_n i'_n = \rho l_f i'_f + e_f - e_n = \rho l_f i'_f + (\eta_n - \eta_f). \quad (7)$$

Dividing both sides of Equation 7 by $i'_f \rho l_n$, we get

$$(i'_n/i'_f) = (l_f/l_n) + (\eta_n - \eta_f)/\rho l_n i'_f. \quad (8)$$

If we now define the secondary current distribution ratio $(i'_n/i'_f) = R$ and divide both sides of Equation 8 by L ,

$$(R/L) = 1 + (\eta_n - \eta_f)/E_f \quad (9)$$

where $E_f = \rho l_f i'_f$.

2.3. The variation of overpotential with current density

In the case of an electrode reaction under activation and concentration polarization, Bockris [14] has shown that

$$i = i_0 \{ (1 - i/i_L) \exp(-\alpha z F \eta / RT) - \exp[(1 - \alpha) z F \eta / RT] \}. \quad (10)$$

When η is sufficiently large ($\eta > 0.05$ V), the dissolution current term (i.e. the second term within the curly brackets of Equation 10), can be neglected and we get

$$i = i_0 [(1 - i/i_L) \exp(-\alpha z F \eta / RT)] \quad (11)$$

or

$$-\eta = b \log_e [(i/i_0)/(1 - i/i_L)] \quad (12)$$

where $b = RT/\alpha z F$. Therefore,

$$-\eta_f = b \log_e [(i'_f/i_0)/(1 - i'_f/i_L)] \quad (13)$$

and

$$-\eta_n = b \log_e [(i'_n/i_0)/(1 - i'_n/i_L)]. \quad (14)$$

Substituting the values of η_f and η_n from Equations 13 and 14 in Equation 9 and rearranging, one gets

$$(R/L) = 1 - (b/E_f) \log_e \{ (i'_n/i'_f) [(i_L - i'_f)/(i_L - i'_n)] \} \quad (15)$$

$$= 1 - (b/E_f) \log_e [(i'_n/i'_f)(1/f)] \quad (16)$$

where

$$f = [(i_L - i'_n)/(i_L - i'_f)].$$

2.4. The approximation of $1 + x \log_e a \approx a^x$

The power series

$$a^x = 1 + x \log_e a + (x^2/L^2)/(\log_e a)^2 + x^3/L^3 \cdot (\log_e a)^3 + \dots \quad (17)$$

can be compared with the geometric series

$$s = 1 + x \log_e a + x^2 (\log_e a)^2 + x^3 (\log_e a)^3 + \dots \quad (18)$$

which is convergent when $x \log_e a$ is less than 1.

Now if we consider each term after the third term of the first series in Equation 17, it will be less

than half of the corresponding terms of the series in Equation 18. If we denote the remainder after the third term of the series in Equation 17 as R_3^1 and that of Equation 18 as R_3^2 , then

$$R_3^1 < R_3^2 \quad (19)$$

and

$$R_3^2 = Y^2/(1 - Y) \quad (20)$$

where $Y = x \log_e a$.

So when the approximation $1 + x \log_e a \approx a^x$ is used, the error involved will be less than

$$[R_3^2/(1 + Y)] 100\% \quad (21)$$

In Table 2, the percentage error involved in such an approximation is tabulated for values of $a = 20, 10$ and 5 and $x = 0.2, 0.1$ and 0.05 . It is evident when $x < 0.1$ that the error is less than 5% for $a = 20, 10$ or 5 . Therefore, using the approximation given by Equation 21 within the limits $a < 20$ and $x < 0.1$ in Equation 16, Equation 16 reduces to

$$(R/L) = (i'_n/i'_f)^{(-b/2.3E_f)} \cdot f^{(b/2.3E_f)} \quad (22)$$

or

$$(R/L) = R^{-K} \cdot f^K$$

where $K = (b/2.3E_f)$

$$\therefore R^{(1+K)} = L \cdot f^K \quad (23)$$

2.5. To express f as a function of L : definition of γ'

In Equation 16, f is defined as equal to $(i_L - i'_n)/(i_L - i'_f)$ and it is evident that f is always a positive fraction because $i_L > i'_n > i'_f$.

At low current densities or at high metal ion concentration in the bath $i_L \gg i'_n > i'_f$ and f tends to 1.

At high current densities i'_n approaches i_L and f tends to zero. But f cannot have a value zero, because by Equation 23 R will then become zero which is not observed in practice. The limiting value of R is $R = 1$.

When $R = 1$, by Equation 23

$$f^K = \frac{1}{L}$$

The limiting value for f is therefore,

$$\frac{1}{L} < f^K < 1 \quad (24)$$

which condition is met with when f is expressed as

$$f = (1/L)^{r/K} \quad \text{with } 0 < r < 1. \quad (25)$$

Thus when r tends to 1, the secondary current distribution is improved; that is throwing power should improve and when it tends to zero the secondary current distribution equals primary current distribution (from Equations 23 and 25).

Now Equation 23 can be written as:

$$R^{(1+K)} = L \cdot f^K = L [(1/L)^{r/K}]^K = L^{(1-r)} \quad (26)$$

or

$$R = L^{[(1-r)/(1+K)]} \quad (27)$$

2.6. The relationship between current efficiency ratio and secondary current distribution ratio: definition of W

If the metal deposition were the only reaction at the cathodes, the metal ratio would be directly equal to the secondary current distribution ratio R . But in the commercial aqueous plating solutions, there is a possibility for the reduction of impurities and addition agents as well as the discharge of hydrogen ions along with metal deposition.

If we denote i_M as the partial current density for the metal discharge and i_H as the partial current density for the parallel cathodic reactions such as hydrogen evolution, reduction of impurities, addition agents etc. then

$$i'_n = i_{Mn} + i_{Hn} \quad (28)$$

and

$$i'_f = i_{Mf} + i_{Hf}$$

The current efficiency by definition will then be given by

$$d_n = (i_{Mn}/i'_n) \quad (29)$$

and

$$d_f = (i_{Mf}/i'_f)$$

Therefore, the ratio of current efficiencies, which is responsible for metal distribution at the cathodes, will be given by

$$(d_n/d_f) = [(i_{Mn}/i'_n)/(i_{Mf}/i'_f)] \quad (30)$$

From Equations 28 and 30

$$(d_n/d_f) = [(i'_n - i_{Hn})/i'_n] [i'_f/(i'_f - i_{Hf})] \\ = [(i'_f/i'_n)] [(i'_n - i_{Hn})/(i'_f - i_{Hf})] \quad (31)$$

When $i_{Hn} \rightarrow i'_n$, i.e. when the current at the near cathode is utilized principally for hydrogen

Table 3. Comparison of metal distribution ratio as calculated by using Equation 36 with experimental values

Solution	Average current density (A dm ⁻²)	W	1-r	b*	E _f (V)	K	M (from Equation 36)	M (experimental)	Error (%)	A	i* (assumed A dm ⁻²)	Reference
Cyanide copper	0.5	0.718	0.9851	0.1984	1.560	0.0553	2.94	2.99	1.7	1.492	2	Haring and Blum [1]
CuCN (0.25 N)												
NaCN (0.60 N)	0.5	0.6663	0.9835	0.4246	1.180	0.1565	3.20	2.91	10	1.402	4	
Na ₂ CO ₃ (0.30 N)												
Linear Ratio L = 5	0.25	0.8135	0.9889	0.2018	0.860	0.102	3.234	3.2	1	1.371	2	
Copper sulphate	1.0	1	0.9927	0.1460	0.800	0.0794	4.395	4.53	2.8	1.087	10	Haring and Blum [1]
CuSO ₄ ·5H ₂ O (1.5 N)												
H ₂ SO ₄	2.0	1	0.992	0.1460	1.593	0.04	4.643	4.63	0.25	1.048	10	
L = 5	1.0	1	0.9975	0.0525	0.687	0.0348	4.719	4.89	3.5	1.038	15	
Air												
21°C	1.0	1	0.9975	0.0610	0.785	0.0338	4.719	4.83	2.28	1.038	15	
Gelatin												
21°C	1.0	1	0.9941	0.1234	0.805	0.0665	4.48	4.48	0	1.074	10	
21°C	0.5	1	0.959	0.1256	0.455	0.12	3.97	4.10	3.2	1.168	10	

* The value of b is taken from [7] and i_L is assumed by the author.

discharge or other reduction processes, the current efficiency ratio tends to zero and when $i_{Hf} \rightarrow i'_f$ there is no deposit at the far cathode (e.g. in chromium deposition). Further, since $i_H < i$ the quantity within the square brackets can never be negative. Hence, this can be expressed as a function of R with limiting values 0 and ∞ . Hence we denote

$$[(i'_n - i_{Hn})/(i'_f - i_{Hf})] = R^W \quad (32)$$

where $-\infty < W < +\infty$, since $R = (i'_n/i'_f)$ is always ≥ 1 . Therefore, from Equations 31 and 32 we get

$$d_n/d_f = \frac{1}{R} \cdot R^W = R^{(W-1)}. \quad (33)$$

2.7. The metal distribution ratio as a function of the primary current distribution ratio

From Equation 30 we get

$$(i_{Mn}/i_{Mf}) = (d_n/d_f)(i'_n/i'_f)$$

i.e.

$$M = \frac{d_n}{d_f} \cdot R. \quad (34)$$

From Equations 33 and 34

$$M = R^{(W-1)}R = R^W. \quad (35)$$

Substituting Equation 27 for R in Equation 35

$$M = \{L^{(1-r)/(1+K)}\}^W = L^{[W(1-r)/(1+K)]} \quad (36)$$

which is of the form $M = L^{1/A}$ proposed by Chin with

$$[W(1-r)]/(1+K) = 1/A, \quad (37)$$

where r is the parameter expressing the influence of concentration polarization and K is the parameter expressing the influence of the Tafel slope b , resistivity of the electrolyte ρ and the current density at the far cathode. The factor W denotes the effect of current efficiency ratio on metal distribution ratio. Qualitatively, that an increase of W , a decrease of r , a decrease in the slope of the current density/potential curve, an increase of electrolyte resistivity and an increase of current density will decrease the throwing power, is evident from Equation 36.

2.8. Verification of Equation 36

The following data are required for the calculation of K , r and W in Equation 36 from the definition

of

$$K = b/2.3E_f = b/2.3\rho l_f i'_f. \quad (\text{Equation 22})$$

$$[(i_L - i'_n)/(i_L - i'_f)] = (1/L)^{r/K} \quad (\text{Equation 25})$$

and

$$(d_n/d_f) = R^{(W-1)}. \quad (\text{Equation 33})$$

From the data given by Haring and Blum, the calculation of M is illustrated below:

2.8.1 Cyanide copper bath.

$L = 5$;

i = the cell current 1 A dm⁻²;

$i'_n = 0.821$ A dm⁻²;

$i'_f = 0.179$ A dm⁻²;

$\rho = 17.4$ Ω cm⁻²;

$b = 0.1984$ (calculated by Gardam);

$i_L = 2$ A dm⁻² (assumed);

$d_n = 49.1\%$;

$d_f = 75.4\%$.

$$(W-1) = (\log d_n - \log d_f)/\log R = \bar{1}.7180,$$

$$\therefore W = 0.7180$$

$$K = b/2.3E_f = b/2.3\rho l_f i'_f$$

$$= 0.1984/2.3 \times 17.4 \times 50 \times 0.00179$$

$$= 0.05539.$$

$$r = -K(\log f/\log L)$$

$$= -0.05531 [\log (1.179/1.821)/\log 5]$$

$$= 0.01494.$$

$$\therefore M = L^{[W(1-r)/(1+K)]} = 5^{(0.7180 \times 0.9851)/1.0553}$$

$$= 5^{0.6702} = 2.941.$$

$$M_{\text{expt}} = 2.990$$

$$A = 1/0.6702 = 1.492.$$

In Table 3, the metal distribution ratio calculated using Equation 36 is compared with the experimental values obtained by Haring and Blum. The close agreement between the calculated values and the experimental results testifies to the validity of Equation 36.

2.9. Comparison of values of 'A' from Equation 36 with the values of 'A' given by Chin

In Table 4, the metal distribution ratio and A calculated using Equation 36 are compared with

Table 4. A comparison of values of metal distribution ratio as calculated by Equation 36 with experimental values and the values of 'A' as calculated by Equation 37 with 'A' found by Chin

Solution	Average current	L	W*	1-r	E _f *	E _f K	M (Equation 36)	M (experimental)	Error (%)	A (by Chin)	A (by Equation 37)	Reference
Cadmium cyanide	1.625	2	0.95	0.9858	1.174	0.0852	1.74	1.825	7.4	1.150	1.254	L.C. Pan [15]
Cd (as metal): 47 g l ⁻¹		3	0.95	0.9847	1.026	0.0973	2.55	2.6	1.9	1.150	1.173	b = 0.23
NaCN (free) 19.5 g l ⁻¹		4	0.95	0.9821	0.84	0.1182	3.173	3.33	4.8	1.150	1.200	assume in comparison with copper
NaOH 27 g l ⁻¹		5	0.95	0.9823	0.854	0.1171	3.820	4.33	12.0	1.150	1.199	cyanide behaviour
Na ₂ CO ₃ 8.5 g l ⁻¹		7	0.95	0.9866	0.496	0.2010	5.236	5.42	3.3	1.150	1.176	i _T = 5 A dm ⁻²
Gulac 20°C No agitation		10	0.95	0.9879	0.538	0.1860	7.22	7.45	3.2	1.150	1.166	assumed by the author
Nickel Watts type	3.0	2	1.024	0.0008	4.321	0.0042	2.025	2.14	5.14	0.920	0.978	*CCE 85-98% ρ = 5.6 ohmcm
NiSO ₄ .7H ₂ O 334 g l ⁻¹		3	1.024	0.0011	3.605	0.0064	3.056	3.23	5.26		0.983	ρ = 11.3 Ω cm
NiCl ₂ .6H ₂ O 36 g l ⁻¹		4	1.024	0.0014	2.558	0.0090	4.08	4.30	5.13		0.986	i _L = 10 A dm ⁻²
Boric acid: 29 g l ⁻¹		5	1.024	0.0012	2.7	0.0085	5.12	5.27	2.85		0.986	assumed by the author
pH 5.5		7	1.024	0.0022	1.424	0.0162	7.082	7.32	3.28		0.995	
Temperature: 32°C		10	1.024	0.002	1.520	0.0152	10.05	10.17	1.2		0.995	
No agitation		20	1.0145	0.9964	0.3699	0.0846	16.33	15.2	7.24	1.073	1.079	Wesley and
Nickel chloride	1	20	1.001	0.9951	0.647	0.0484	17.18	16.2	6.0	1.053	1.070	Roehl [16]
NiCl ₂ .6H ₂ O 300 g l ⁻¹		4	1.008	0.9777	1.264	0.0248	18.71	17.3	8.1	1.023	1.046	ρ = 5.4 Ω cm
Total Ni 75 g l ⁻¹		1	1.0124	0.9981	0.945	0.0331	4.826	4.48	7.8	1.025	1.079	b = 0.072
Boric acid: 30 g l ⁻¹		2	1.006	0.9970	1.336	0.0234	4.84	4.62	2.6	1.020	1.070	i _L = 15 A dm ⁻²
pH 2.0		4	1.006	0.9973	3.645	0.0089	4.96	4.77	4.98	1.01	1.046	assumed by the author

the experimental values of metal distribution ratio reported [15, 16] and the value of A from the slope of the $\log M - \log L$ plot by Chin. This exemplifies the value of logarithmic throwing index as well as the validity of Equation 36 derived above, in spite of the fact that missing data for the calculation of M in certain cases have to be compiled from different sources.

3. Summary

The logarithmic throwing index A derived by Chin empirically from the plot of $\log M$ versus $\log L$ is shown to be a function of K , r and W where K is related to the activation polarization, r is related to the concentration polarization and W is related to the ratio of current efficiencies. The validity of the equation $M = L^{[W(1-r)/1+K]}$ has been checked with the data from published results from different sources and it is found that the metal distribution ratio calculated by the above formula is within 10% of the experimentally observed values. That the logarithmic throwing index can be used as a single valued parameter for measuring throwing power of electrolytes over a range of Linear Ratios has a theoretical basis, is also proved. It is also shown that A can be calculated with reasonable accuracy from experimentally measurable quantities using a Haring-Blum type of cell, if the data, the current density-potential curve, current density-current efficiency curve and the specific resistance of the electrolyte are available.

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